

TITLE OF THE INVENTION

SYNTHETIC GAS MANUFACTURING PLANT AND SYNTHETIC GAS
MANUFACTURING METHOD

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application is based upon and claims the
benefit of priority from the prior Japanese Patent
Application No. 2002-332719, filed November 15, 2002,
the entire contents of which are incorporated herein by
reference.

10 BACKGROUND OF THE INVENTION

1. Field of the Invention

 The present invention relates to a synthetic gas
manufacturing plant and a synthetic gas manufacturing
method used in, e.g., synthesis of methanol, synthesis
15 of dimethylether, or synthesis of gasoline, kerosene,
and light oil in a Fischer-Tropsch reaction system.

 More specifically, the present invention relates
to an energy-saving synthetic gas manufacturing plant
and method which use carbon dioxide produced in the
20 system as the material of a synthetic gas, which
contributes to the prevention of global warming by
discharging no residue to the atmosphere even if a
residue is produced, and which can effectively use heat
generated in the system.

25 2. Description of the Related Art

 A synthetic gas mainly containing hydrogen (H₂)
and carbon monoxide (CO) is used in, e.g., synthesis of

methanol, dimethylether (DME), or gasoline in the GTL (Gas To Liquid) process in a Fischer-Tropsch reaction system.

Jpn. Pat. Appln. KOKAI Publication No. 2001-97905
5 discloses a method of manufacturing a synthetic gas by supplying a natural gas and carbon dioxide recovered from a combustion exhaust gas from a reformer to a moistening device, adding steam to this moistening device to prepare a source gas containing the
10 steam-added gas mixture, and supplying this source gas to the reformer to cause a reforming reaction.

This synthetic gas manufacturing method recovers part of carbon dioxide from the combustion exhaust gas produced in the reformer, and uses the recovered carbon
15 dioxide as the source gas of a synthetic gas. This increases the production of the synthetic gas, and also reduces the amount of carbon dioxide discharged from a chimney to the atmosphere, thereby contributing to the prevention of global warming.

20 Recently, as one measure to counter the global warming phenomenon, it is being strongly desired to minimize the amount of that carbon dioxide discharged to the atmosphere, which is produced when fossil fuel or the like is combusted.

25 Unfortunately, in the conventional synthetic gas manufacturing method, a considerable amount of combustion exhaust gas containing carbon dioxide

produced in the reformer is discharged from a chimney to the atmosphere.

BRIEF SUMMARY OF THE INVENTION

5 It is an object of the present invention to provide a synthetic gas manufacturing plant and synthetic gas manufacturing method, which greatly contribute to preservation of the global environment by discharging no carbon dioxide to the atmosphere.

10 It is another object of the present invention to provide an energy-saving synthetic gas manufacturing plant and synthetic gas manufacturing method by which heat generated in the system is effectively used in the system, thereby minimizing the amount of heat discharged outside the system.

15 According to an aspect of the present invention, there is provided a synthetic gas manufacturing plant comprising:

20 a reformer having a reaction tube, a combustion radiation unit arranged around the reaction tube to heat the reaction tube, and a convection unit communicating with the combustion radiation unit;

a source gas supply passageway to supply a natural gas to the reformer;

25 a steam supply passageway to supply steam to the source gas supply passageway;

a carbon dioxide recovery apparatus to which a total amount of combustion exhaust gas flowing through

the convection unit of the reformer is supplied, and which recovers carbon dioxide from the combustion exhaust gas;

5 a compressor to compress the recovered carbon dioxide; and

a return passageway to supply part or the whole of the compressed carbon dioxide from the compressor to the source gas supply passageway.

10 According to another aspect of the present invention, there is provided a synthetic gas manufacturing method comprising steps of:

providing a synthetic gas manufacturing plant which comprises

15 (a) a reformer having a reaction tube, a combustion radiation unit arranged around the reaction tube to heat the reaction tube, and a convection unit communicating with the combustion radiation unit,

(b) a source gas supply passageway to supply a natural gas to the reformer,

20 (c) a steam supply passageway to supply steam to the source gas supply passageway,

(d) a carbon dioxide recovery apparatus to which a total amount of combustion exhaust gas flowing through the convection unit of the reformer is supplied, and
25 which recovers carbon dioxide from the combustion exhaust gas,

(e) a compressor to compress the recovered carbon

dioxide, and

(f) a return passageway to supply part or the whole of the compressed carbon dioxide from the compressor to the source gas supply passageway;

5 recovering, by the carbon dioxide recovery apparatus, carbon dioxide in the total amount of combustion exhaust gas which is exhausted from the combustion radiation unit of the reformer, and flows in the convection unit;

10 compressing the carbon dioxide recovered by the carbon dioxide recovery apparatus by the compressor; and

supplying part or the whole of the compressed carbon dioxide to the source gas supply passageway through the return passageway, and supplying steam to the source gas supply passageway through the steam supply passageway, thereby supplying a gas mixture of the natural gas, compressed carbon dioxide, and steam, as a source gas, to the reaction tube externally heated by the combustion radiation unit of the reformer.

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Additional objects and advantages of the invention will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out hereinafter.

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BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate presently preferred embodiments of the invention and, together with the generation description given above and the detailed description of the preferred embodiments given below, serve to explain the principles of the invention.

FIG. 1 is a schematic view showing the main parts of synthetic gas manufacture used in an embodiment of the present invention;

FIG. 2 is a schematic view showing a carbon dioxide recovery apparatus incorporated into FIG. 1; and

FIG. 3 is a schematic view showing the major parts of synthetic gas manufacture used in another embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

A synthetic gas manufacturing plant and a synthetic gas manufacturing method according to the present invention will be described in detail below with reference to the accompanying drawing.

FIG. 1 is a schematic view showing a synthetic gas manufacturing plant according to this embodiment.

FIG. 2 is a schematic view showing a carbon dioxide recovery apparatus incorporated into the synthetic gas manufacturing plant shown in FIG. 1.

A reformer 10 includes a steam reforming reaction tube 11, a combustion radiation unit 12 formed around the reaction tube 11, and a convection unit (waste heat recovering unit) 13 connected to the combustion radiation unit 12. The reformer 10 communicates with a chimney 14. In the convection unit 13, a flow path area varying means (e.g., a damper 15) is placed downstream of the diverging point of a combustion exhaust gas supply passageway (to be described later). The reaction tube 11 is filled with a catalyst (e.g., a nickel-based catalyst) for forming a synthetic gas.

A fuel supply passageway 20₁ is connected to the combustion radiation unit 12 of the reformer 10. A source gas supply passageway 20₂ is connected to the upper end of the reaction tube 11 via the convection unit 13 of the reformer 10. A desulfurization unit (not shown) can also be inserted into the passageway 20₂. A steam supply passageway 20₃ is connected to the upstream side before the intersection of the source gas supply passageway 20₂ and the convection unit 13. A passageway 20₄ in which a fluid to be heated, e.g., boiler water flows intersects the convection unit 13 of the reformer 10. Heat is exchanged between the combustion exhaust gas in the convection unit 13 and the boiler water, so the combustion exhaust gas is cooled, and the boiler water is heated to produce steam. This steam is supplied to a steam turbine (to

be described later). By changing the pressure of the boiler water or the heat exchange conduction area, medium-pressure steam or high-pressure steam can be supplied in accordance with the needs on the steam turbine side. To use part of this steam in the synthesis of a synthetic gas, the steam may also be supplied to the source gas supply passageway 20₂ through the steam supply passageway 20₃.

A synthetic gas passageway 20₅ is connected to the lower end of the reaction tube 11 of the reformer 10. A heat exchanger 31 is inserted into the synthetic gas passageway 20₅, and a passageway 20₆ intersects the heat exchanger 31. The heat exchanger 31 heats a fluid to be heated, e.g., boiler water flowing in the passageway 20₆, thereby producing steam. This steam is supplied to the steam turbine (to be described later). By changing the boiler water pressure or the heat exchange conduction area, medium-pressure steam or high-pressure steam can be supplied in accordance with the needs on the steam turbine side.

A carbon dioxide recovery apparatus 40 is connected to the convection unit 13 of the reformer 10 through a combustion exhaust gas supply passageway 20₇, and the total amount of combustion exhaust gas flowing in the convection unit 13 is supplied. As shown in FIG. 2, the carbon dioxide recovery apparatus 40 includes a cooling tower 41, carbon dioxide absorption

tower 42, and absorbing solution regeneration tower 43 arranged adjacent to each other. The cooling tower 41 incorporates a gas-liquid contacting member 44. The carbon dioxide absorption tower 42 incorporates

5 gas-liquid contacting members 45a and 45b. The gas-liquid contacting member 45a efficiently brings combustion exhaust gas containing carbon dioxide into contact with an absorbing solution for removing carbon dioxide from the combustion exhaust gas by absorption.

10 The gas-liquid contacting member 45a is placed above an overflow portion 46 of the regenerated absorbing solution. The gas-liquid contacting member 45b having the same function is placed below the overflow portion 46. The absorbing solution regeneration tower 43
15 incorporates two, upper and lower gas-liquid contacting members 47a and 47b.

The cooling tower 41 is connected to the convection unit 13 through the combustion exhaust gas supply passageway 207. When the convection unit 13 is
20 totally closed downstream of the diverging point of the combustion exhaust gas supply passageway 207 by the damper 15 formed in the convection unit 13, the total amount of the combustion exhaust gas is supplied to the carbon dioxide recovery apparatus 40. By adjusting the
25 opening of the damper 15, the combustion exhaust gas may also be entirely or partially discharged outside the system from the chimney 14, without being supplied

to the carbon dioxide recovery apparatus 40, in accordance with the maintenance or failure of the carbon dioxide recovery apparatus 40, or some other situation.

5 Cooling water is sprayed from the upper portion of the cooling tower 41 through a passageway 20₈, and efficiently brought into contact with a combustion exhaust gas supplied through the combustion exhaust gas supply passageway 20₇ by the gas-liquid contacting
10 member 44, thereby cooling the combustion exhaust gas. The top of the cooling tower 41 is connected to a portion near the bottom of the carbon dioxide absorption tower 42 through a passageway 20₉. A blower 48 is inserted into the passageway 20₉.

15 The bottom of the absorption tower 42 is connected through a passageway 20₁₀ to a position between the two, upper and lower gas-liquid contacting members 47a and 47b of the absorbing solution regeneration tower 43. A pump 49 and heat exchanger 50 are inserted into
20 the passageway 20₁₀ in this order from the side of the absorption tower 42.

 The bottom of the absorbing solution regeneration tower 43 is connected to the upper portion of the absorption tower 42 where the overflow portion 46
25 exists, through a passageway 20₁₁ into which the heat exchanger 50 is inserted. A pump 51 is inserted into the passageway 20₁₁ between the bottom of the absorbing

solution regeneration tower 43 and the heat exchanger 50. One end of a passageway 20₁₂ is connected to the overflow portion 46 of the absorption tower 42, and the other end of the passageway 20₁₂ is connected to a
5 position above the upper gas-liquid contacting member 45a of the absorption tower 42 via a pump 52. A heat exchanger 56 is inserted into the passageway 20₁₂. One end of an exhaust passageway 20₁₃ is connected to the top of the absorption tower 42, and the other end of
10 the exhaust passageway 20₁₃ is connected to the convection unit 13 of the reformer 10.

One end of a passageway 20₁₄ is connected to a portion near the bottom of the absorbing solution regeneration tower 43, and the other end of the
15 passageway 20₁₄ is connected to a portion immediately below the gas-liquid contacting member 47b of the absorbing solution regeneration tower 43. A pump 53 and heat exchanger 54 are inserted into the passageway 20₁₄ in this order from the portion near the bottom of
20 the absorbing solution regeneration tower 43. A passageway 20₁₅ in which low-pressure steam from the steam turbine (to be described later) flows intersects the heat exchanger 54. Accordingly, this low-pressure steam exchanges heat with a regenerated solution
25 flowing through the passageway 20₁₄ and condenses. One end of a passageway 20₁₆ is connected to the top of the regeneration tower 43, and the other end of the

passageway 20₁₆ is connected to a compressor (to be described later) via a cooling heat exchanger 55. A passageway 20₁₇ connected to a portion above the upper vapor-liquid contacting member 47a in the regeneration tower 43 branches from the passageway 20₁₆ on the downstream side of the cooling heat exchanger 55.

A compressor 62 driven by a steam turbine 61 is connected to the carbon dioxide recovery apparatus 40 through the passageway 20₁₆. The compressor 62 is connected to the source gas supply passageway 20₂ on the upstream side of the reformer 10 via a return passageway 20₁₈. A passageway 20₁₉ for discharging compressed carbon dioxide outside the system branches from the return passageway 20₁₈.

The passageways 20₄ and 20₆ in which the steam flows are connected to the steam turbine 61. The steam turbine 61 is connected to the low-pressure steam passageway 20₁₅ intersecting the heat exchanger 54 of the carbon dioxide recovery apparatus 40.

The synthetic gas manufacturing method of the present invention will be described below with reference to the synthetic gas manufacturing plant shown in FIGS. 1 and 2.

First, combustion fuel is supplied to the combustion radiation unit 12 of the reformer 10 through the fuel supply passageway 20₁. In the combustion radiation unit 12, the combustion fuel is combusted

together with air to heat the reaction tube 11 to a predetermined temperature. The combustion exhaust gas produced in the combustion radiation unit 12 to heat the reaction tube 11 to a predetermined temperature
5 flows into the convection unit 13. Since the source gas supply passageway 20₂ intersects the convection unit 13, a source gas flowing through the source gas supply passageway 20₂ is preheated, and at the same time the combustion exhaust gas is cooled. Also, since
10 the passageway 20₄ intersects the convection unit 13, heat is exchanged between the combustion exhaust gas and boiler water flowing through the passageway 20₄. Consequently, the boiler water turns into medium-pressure or high-pressure steam, and at the same time
15 the combustion exhaust gas is cooled.

When the convection unit 13 and the chimney 14 are separated by the damper 15, the combustion exhaust gas whose heat is partially recovered by the boiler water and the like is entirely supplied to the cooling tower
20 41 of the carbon dioxide recovery apparatus 40 through the combustion exhaust gas supply passageway 20₇. In the cooling tower 41, the gas-liquid contacting member 44 efficiently cools the supplied combustion exhaust gas by gas-liquid contact with cooling water which is
25 supplied through the passageway 20₈ and sprayed. The cooled combustion exhaust gas is supplied from the top of the cooling tower 41 to a portion near the bottom of

the carbon dioxide absorption tower 42 through the passageway 20₉ by the blower 48. While the combustion exhaust gas rises in the lower gas-liquid contacting member 45b in the carbon dioxide absorption tower 42, 5 the combustion exhaust gas comes in contact with a regenerated absorbing solution, for example a regenerated amine solution, supplied from the absorbing solution regeneration tower 43 to the upper portion of the gas-liquid contacting portion of the absorption 10 tower 42 through the passageway 20₁₁ via the heat exchanger 50. As a consequence, carbon dioxide in the combustion exhaust gas is absorbed by the regenerated amine solution. The combustion exhaust gas further passes through the overflow portion 46 and the upper 15 gas-liquid contact member 45a. During this process, the combustion exhaust gas comes into contact with the regenerated amine solution, which is supplied to the portion near the top of the absorption tower 42 through the passageway 20₁₂ with the help of the function of 20 the pump 52. As a result, CO₂ of the combustion exhaust gas remaining unabsorbed is absorbed. At this time, the combustion exhaust gas heated by carbon dioxide gas absorption is cooled by the regenerated amine solution, which is cooled by heat exchanger 56 25 inserted the passageway 20₁₂.

This combustion exhaust gas from which carbon dioxide is removed is supplied to the chimney 14

through the exhaust passageway 20₁₃ and discharged outside. A carbon dioxide absorbing solution, for example a carbon dioxide absorbing amine solution, is stored in the bottom of the absorption tower 42, and
5 supplied to a portion between the two gas-liquid contacting members 47a and 47b of the absorbing solution regeneration tower 43 through the passageway 20₁₀ by the pump 49. While the carbon dioxide absorbing amine solution flows through the heat
10 exchanger 50 inserted into the passageway 20₁₀, heat is exchanged between this amine solution and a regenerated amine solution at a relatively high temperature flowing through the passageway 20₁₁ connected to the bottom of the regeneration tower 43. Consequently, the carbon
15 dioxide absorbing amine solution is heated, and the regenerated amine solution is cooled. The heated carbon dioxide absorbing amine solution is separated into carbon dioxide and a regenerated amine solution, as it flows down in the lower gas-liquid contacting
20 member 47b in the regeneration tower 43. The regenerated amine solution stored in the bottom of the regeneration tower 43 is circulated through the passageway 20₁₄ by the pump 53, and heated by heat exchange by the heat exchanger 54 intersected by the
25 passageway 20₁₅ in which low-pressure steam exhausted from the steam turbine (to be described later) flows. Consequently, the regeneration tower 43 itself is

heated and used as the heat source of separation between carbon dioxide and a regenerated amine solution.

5 The regenerated amine solution is stored in the bottom of the regeneration tower 43, and returned to the absorption tower 42 through the passageway 20₁₁ by the pump 51. The carbon dioxide rises in the upper gas-liquid contacting member 47a and is discharged from the top of the regeneration tower 43 through the
10 passageway 20₁₆. During the process, the carbon dioxide is cooled in the cooling heat exchanger 55, and the steam and amine steam carried together with this carbon dioxide are condensed. The condensed water is returned to the regeneration tower 43 through the
15 branched passageway 20₁₇.

After carbon dioxide in the combustion exhaust gas is recovered by the carbon dioxide recovery apparatus 40, this carbon dioxide is supplied to the compressor 62 through the passageway 20₁₆. Steam generated by
20 heat exchange at the intersection with the convection unit 13 of the reformer 10 and steam generated by heat exchange by the heat exchanger 31 (to be described later) are supplied to the steam turbine 61 through the passageways 20₄ and 20₆ and drive the steam turbine 61.
25 The steam turbine 61 drives the compressor 62, and carbon dioxide supplied to the compressor 62 is compressed. When steam is generated by exchanging heat

with the combustion exhaust gas, medium-pressure steam or high-pressure steam can be supplied in accordance with the needs on the steam turbine side, by changing the boiler water flow rate, heat exchange conduction
5 area, or the like.

A portion of the compressed carbon dioxide can be supplied through the return passageway 20₁₈ to the passageway 20₂ in which a natural gas flows, and used as the raw material of a synthetic gas. The remaining
10 compressed carbon dioxide can be discharged outside the system (e.g., to a urea plant or into the ground) through the return passageway 20₁₈ and passageway 20₁₉.

The low-pressure steam exhausted from the steam turbine 61 is supplied to the carbon dioxide recovery
15 apparatus 40 through the passageway 20₁₅. The heat exchanger 54 performs heat exchange between this low-pressure steam and the regenerated amine solution circulated through the passageway 20₁₄. As a consequence, the regenerated amine solution is heated,
20 and the low-pressure steam is cooled into condensed water. This condensed water is returned as the boiler water described above to the passageways 20₄ and 20₆ through the passageway 20₁₅.

A natural gas mainly containing methane is
25 supplied to the source gas supply passageway 20₂. A predetermined amount of carbon dioxide compressed by the compressor 62 is added through the return

passageway 20₁₈ to the natural gas which flows in the source gas supply passageway 20₂. Also, a predetermined amount of steam is added to the natural gas through the steam supply passageway 20₃. This steam
5 can be generated by exchanging heat between boiler water and a synthetic gas in the heat exchanger 34, or generated by exchanging heat between boiler water and a combustion exhaust gas in the convection unit 13 of the reformer 10.

10 The natural gas to which the carbon dioxide and steam are added flows in the source gas supply passageway 20₂, and is heated while passing through the convection unit 13 of the reformer 10. The heated natural gas is supplied to the reaction tube 11. Of
15 the natural gas mainly containing methane (CH₄), the steam, and the carbon dioxide supplied to the reaction tube 11 of the reformer 10, primarily methane is subjected to steam reforming in the presence of a catalyst in the reaction tube 11, thereby manufacturing
20 a synthetic gas containing hydrogen, carbon monoxide, and carbon dioxide. This reforming reaction is an endothermic reaction. As described previously, therefore, a fuel gas and air are combusted in the combustion radiation unit 12 of the reformer 10 to heat
25 the reaction tube 11 to, e.g., 850 to 900°C. The obtained synthetic gas is supplied to the heat exchanger 31 through the synthetic gas passageway 20₅.

This synthetic gas heats the boiler water flowing through the passageway 20₆ to generate steam, and the synthetic gas itself is cooled. The steam is supplied to the steam turbine 61 and drives it.

5 In the embodiment of the present invention as described above, when a synthetic gas containing hydrogen and carbon monoxide is to be manufactured by the reforming step of supplying a source gas containing a natural gas and steam to the reformer 10, carbon
10 dioxide contained in the total amount of combustion exhaust gas produced in the reformer 10 is recovered by the carbon dioxide recovery apparatus 40. This carbon dioxide is supplied to the compressor 62 and compressed by driving the compressor 62 by using a heat source
15 generated in the reforming step. More specifically, steam generated by heat exchange at the intersection with the convection unit 13 of the reformer 10 and steam generated by heat exchange in the heat exchanger 31 are supplied to the steam turbine 61 through the
20 passageways 20₄ and 20₆ and drive the steam turbine 61. By driving the compressor 62 by the driving force of the steam turbine 61, carbon dioxide can be compressed by excess steam generated in the reforming step.

 A portion of this compressed carbon dioxide is
25 supplied to the natural gas and steam, and a source gas containing this compressed carbon dioxide is supplied to the reaction tube 11 of the reformer 10 to cause a

reforming reaction, thereby increasing the production of the synthetic gas. Also, in accordance with a failure of the carbon dioxide recovery apparatus 40 or some other situation, the combustion exhaust gas can be
5 entirely or partially discharged outside the system from the chimney 14, without being supplied to the carbon dioxide recovery apparatus 40, by adjusting the opening of the damper 15.

On the other hand, if the amount of compressed
10 carbon dioxide is excessive compared to the amounts of natural gas and steam, the compressed carbon dioxide can be effectively used in installations outside the system. Furthermore, this compressed carbon dioxide may also be discharged to and fixed in the ground such
15 as an oil field.

Accordingly, the production of the synthetic gas can be increased. In addition, the excess heat source in the reforming step can be effectively used, e.g., steam can be generated by this excess heat and supplied
20 to the steam turbine. Also, the amount of carbon dioxide discharged from the chimney can be reduced to substantially zero. This makes it possible to improve the economical efficiency by reducing the carbon dioxide discharge tax, and contribute to the prevention
25 of global warming.

The obtained synthetic gas can be used in synthesis of gasoline or the like in a Fischer-Tropsch

reaction system, synthesis of methanol, or synthesis
of dimethylether. If the synthetic gas is to be
applied to synthesis of gasoline or the like in a
Fischer-Tropsch reaction system, the synthetic gas
5 preferably has a composition in which the molar ratio
of H_2/CO is 1 to 2.0.

In the above embodiment, as shown in FIG. 1, a
combustion exhaust gas is supplied from the convection
unit 13 to the carbon dioxide recovery apparatus 40
10 through the passageway 207. However, as shown in
FIG. 3, this combustion exhaust gas may also be
directly supplied from the convection unit 13 to the
carbon dioxide recovery apparatus 40 (the cooling tower
41 shown in FIG. 2), so that the total amount of
15 combustion exhaust gas is always processed.

Additional advantages and modifications will
readily occur to those skilled in the art. Therefore,
the invention in its broader aspects is not limited to
the specific details and representative embodiments
20 shown and described herein. Accordingly, various
modifications may be made without departing from the
spirit and scope of the general inventive concept as
defined by the appended claims and their equivalents.